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Of the molecules measured with EFISH there is a striking constancy of their microbeta products and even the more approximate beta's themselves. These molecules are all nitrobenzene derivatives and the observation could be made that the magnitude of beta is more or less tied to this conjugated portion of the molecules. Comparison of the power data with the molecular hyperpolarizabilities illustrates that a study of powder response tells essentially nothing whatever about molecular properties. Attention should be directed to crystal studies in the search for materials destined for application to the processing of weak optical signals.

The dependence of molecular polarizability on concentration in some solvents for some solutes at very low concentrations has not been clearly seen before. These measurements were all made on solutions of less than 1 molecular percent and so solute-solute interaction almost certainly is absent. Two compounds, ANDS, and ClHgNa look promising. Measurements made on some newly synthesized ruthenium (II) n5-cyclopentadienyl n6-arene salts as powders

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demonstrated a rather low frequency doubling efficiency and a photolytic sensitivity that would not suit them for future practical applications. It is to be noted, however, that the more difficulty synthesizable analogues, having donor and acceptor groups separated by the ruthenium atom, have not been attained.

FINAL TECHNICAL REPORT

AFOSR·TR· 87-1180

"NEW ORGANIC AND ORGANOMETALLIC MATERIALS WITH NONLINEAR

OPTICAL PROPERTIES FOR OPTICAL SIGNAL PROCESSING"

September 1, 1984 to September 30, 1986

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I.   Introduction

The goals of this research were the discovery of materials effective in second harmonic generation, SHG, and other non-linear optical effects. These materials must possess other properties that are superior to those of crystals in current use. These properties are: efficiency in optical processing, broad wavelength transmission range, resistance to high-power damaging radiation, and ease of growth of near perfect crystals. There was a specific interest in organometallic compounds; these promising classes have not received much previous attention. The plans called for the determination of molecular nonlinear polarizabilities in solution by electric field induced second harmonic generation (EFISH) and subsequent growth of crystals that benefit from optimum alignment of the molecular directions of highest polarizability. This latter was to be accomplished by suitable substitution and other chemical manipulations of the organic parts of the molecules and by replacements of the metal ions. Comparison of the second harmonic response of the materials as powders with EFISH measurements of their solutions was to guide the preparative aspects.

Obviously, a program that involves the setting up and staffing of a new laboratory, the preparation of new compounds, the growth of crystals, the analysis of crystal structures, and the perfection of the decidedly non-trivial EFISH experiment could not be up and running in a short period of time. Indeed, the coinvestigators expected that the sponsors were sufficiently interested in the results of this program to plan funding for several terms of three years each. Their experience over a combined career of sixty years of government sponsorship has born out the logic of this expectation. Cessation of support after only two years has made it difficult to continue a program that the investigators had devoted a great deal of time and effort to launch.

II. Brief Review of Theory

The work had a very definite goal, that of surveying certain classes of solid crystalline materials for their efficiencies in non-linear optical devices. Important examples of such devices are second harmonic generators (SHG), tunable parametric oscillators, electrooptic modulators and other optical signal processors. The property of the materials which signals their possible effectiveness for such devices is the non-linear optical coefficient d_{ijk}, an element of a third rank tensor often symbolized by $\chi^{(2)}$ defined by

or

$$\vec{P} = \chi^{(1)} \vec{E} + \chi^{(2)} \vec{E}\vec{E} + \chi^{(3)} \vec{E}\vec{E}\vec{E} + \ldots$$

$$P_i = \epsilon_0 \left[\sum_j \chi_{ij} E_j + 2 \sum_{j,k} d_{ijk} E_j E_k + \ldots \right]$$

(1)

Here P_i is one cartesian component of the bulk polarization of the medium under the influence of the three cartesian electric field components E_i, ϵ_0 is the electric permeability of a vacuum, and χ_{ij} is an (second rank tensor) electric susceptibility component. Since the interchange of j and k in equation (1) has no physical significance, the number of different components d_{ijk} immediately reduces from 27 to 18, and further demands of the crystallographic point symmetry groups drastically reduce the number of independent components in practical cases. The widely used SHG crystal KH_2PO_4 (KDP), for example, has only one non-zero component; centrosymmetric crystal classes have all $d_{ijk}=0$. Where single crystal work on SHG has accomplished determination of different non-linear coefficients, at most three have been measured.[1] These, moreover, are usually comparable in magnitude, so that an average $\hat{d}$ will be a good measure of SHG efficiency. These observations suggested the use of non-oriented samples for testing $\hat{d}$, that is, crystalline

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powders.[2,3] There exist interrelationships between all nonlinear optical properties so that many other such properties are capable of being deduced from results of measurements of SHG efficiency.

Preliminary surveying should, in view of the time-consuming complexities of large, single crystal work, be carried out on disoriented samples. Promising materials must then be treated to more refined measurements. Besides the magnitude of d_{ijk}, the operation of a nonlinear device depends upon the principal refractive indices including wavelength dispersion, the optical transmission range, the sensitivity to optical damage from high laser fields, the optical perfectability, chemical stability (and reactivity) and phase matching characteristics. This last requirement stems from the obvious notion that in the crystal the longer the distance that the field at frequency ω remains in phase with the field at 2ω, which it is generating, the larger the amplitude and intensity at 2ω and the more efficient the energy up-conversion. Some materials cannot be phase-matched ($n_{2\omega} = n_{\omega}$), but where this is possible substantial increases in the SHG intensity is observed. Phase matching may often be accomplished in birefringent crystals where, for a certain angle of the wave vector with respect to the optic axis, the ordinary ray of frequency ω has the same refractive index as the extraordinary ray at 2ω. This is because $n_{(ext)}^{2\omega}$ is "tunable" by this angle and can be "tuned" to equal $n_{(ord)}^{\omega}$. It may be at first surprising that a study of SHG efficiency vs particle size of powders definitively tells whether or not phase matching would be possible with suitably oriented single crystals.[2]

While nonlinear optical phenomena in solids depend upon the tensor $\chi^{(2)}$ in equation (1) the magnitude of these components obviously is related to corresponding properties of the molecules or ions in the crystal (and intermolecular interactions). The microscopic analogy to equation (1) is

or

$$\vec{p} = \underset{\sim}{\alpha}\vec{E} + \underset{\sim}{\beta}\vec{E}\vec{E} + \gamma\vec{E}\vec{E}\vec{E} + \ldots$$

$$P_i = \sum_j \alpha_{ij}E_j + \sum_{j,k} \beta_{ijk}E_jE_k + \sum_{j,k,l} \gamma_{ijkl}E_jE_kE_l + \ldots \qquad (2)$$

in which p_i is the ith component of the induced dipole moment, $\underset{\sim}{\alpha}$ is the second rank polarizability tensor and β and γ are the third and fourth rank "hyper-polarizability" tensors. For $\chi^{(2)}$ to be non-vanishing, β also must be differ-ent from zero, but, of course, the inverse is not true because molecular orientation (as in crystalline centrosymmetry) can provide cancellation.

Light can be thrown on the components of β by measurements in the gas phase and solutions. The latter have usually been preferred because of low vapor pressure of active compounds. Solutions have a statistically centrosym-metric structure, but a DC field can be impressed to remove this symmetry. The measured polarization is then related to the average microscopic polariza-tion of the molecules in the liquid at the frequency of the second harmonic, that due to β and γ. These angularly averaged molecular second and third order hyperpolarizabilities are related in a straightforward way to the components of the corresponding tensors.[4] Contributions from solute-solvent interactions can be eliminated by taking data at different concentrations and extrapolating to infinite dilution.[5]

Interpretation of the DC-induced SHG (or EFISH) in terms of the molecular hyperpolarizabilities deserves a short discussion. On the molecular scale the harmonic polarization,[4]

$$P_i^{2\omega} = \sum \beta_{ijk}E_j^\omega E_k^\omega + \sum \gamma_{ijkl}^e E_j^\omega E_k^\omega E_l^o + \sum_\sigma \xi_{ijk\sigma}E_j^\omega E_k^\omega Q_\sigma. \qquad (3)$$

$$\quad\text{rotational}\quad\quad\text{electronic}\quad\quad\text{vibrational}$$

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The indices i,j,k are molecule-fixed cartesians, E_j^ω is an effective amplitude at the molecule, ω and 2ω are frequencies and E_ℓ° refers to the DC field. Q_σ is the normal coordinate of the σth vibrational mode, the β_{ijk} are the components of the second order hyperpolarizability tensor while the γ_{ijkl}^e are the components of the third order hyperpolarizability tensor. The $\xi_{ijk,\sigma}$ are the hyper-Raman susceptibilities for vibrational modes σ. Now the total <u>measured</u> nonlinearity of the liquid $\Gamma = M \gamma f_o f_\omega^2 f_{2\omega}$ [$P^{2\omega} = \Gamma E^\circ (E^\omega)^2$ by analogy to eq. (1)] in which the field factors f are obtained from solution theory and relate the applied fields at o, ω, 2ω to the local fields at the molecules. Small γ in this equation is the total, averaged hyperpolarizability, $\gamma = \gamma^e + \gamma^v + \gamma^r$ (for electronic, vibrational, and rotational contributions), which can be mapped into correspondence with equation (3). This requires orientational averaging of $p_i^{2\omega}$, discarding of tensor components considered to be of secondary importance, and applying symmetry rules to those that are left. It turns out that,[6]

$$\gamma = \gamma^e + \frac{\mu\beta}{5kT} , \tag{4}$$

in which β is the projection of the vector part of the nonlinear hyper- polarizability tensor along the dipolar axis of the molecule.

The two terms in equation (4) can be determined separately by using a different non-linear experiment on the electronic part, a four wave mixing technique[7], but, in general, γ^e is negligibly small in comparison with the second term.

EFISH can thus be used to judge the microscopic hyperpolarizability, β, and molecules can be designed and constructed to maximize this parameter. However, this is still a long way from the fabrication of highly efficient nonlinear crystals, because crystal structures are determined by packing

forces that could well provide cancellation of the β tensors. As an example, high electric dipole moments usually accompany large β's, but polar molecules usually crystallize in centrosymmetric classes so as to minimize dipolar repulsions. Nevertheless, the two techniques for determining β in solution and $\chi^{(2)}$ of crystals by the rapid powder method can be used together. One would certainly not attempt to synthesize molecules with low values of β, and there are synthetic tricks for coaxing crystallization into space groups of low symmetry. An example is to induce a "handedness" by the employment of chiral subunits. An ideal limiting value of $\chi^{(2)}$ can be determined from any β and a maximum approach to this ideal can be sought by synthetic slyness. Skillful use of hydrogen bonding has, for example, been employed.[8]

Research of the nature described above has so far been done on organic materials with polarizable π electron systems, both mono- and polymeric. Startling improvements over the standard inorganic crystals have been seen. For example, 2-methyl-4-nitroaniline has 50 times the SHG power of potassium dihydrogen phosphate. Most of the organics studied also have a greater resistance to damage from the high optical pump fields. One serious problem with the designing of conjugated π system molecules is that as the conjugation and polarizabilities (hyper as well as normal) increase, the electronic absorption frequency decreases, often pushing down into the frequency range of the desired second harmonic of some convenient fundamental wavelength.

During the first year of this research equipment was assembled for the EFISH measurements in solution, and about 200 solids were tested as powders for frequency doubling of the 1.064 μm Nd:YAG laser fundamental. A post-doctoral physical chemist was hired for this work, however, a suitable preparative organic chemist was not available until the second year. Most classes of organic compounds were exemplified in the study, with particular attention

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devoted to crystals whose molecular components possessed low lying charge transfer spectral transitions, as this had been found years ago to enhance molecular hyperpolarizabilities and should be mirrored in high second order electric susceptibilities if the molecules are "correctly" aligned in the crystal. Because centrosymmetrical crystal point groups must have vanishing even order susceptibilities many optically active materials were tested.

This experiment consisted simply of confining the powdered materials between glass plates and, with a phototube, observing the harmonic at $0.532\ \mu m$ resulting from the impinging of an unfocussed laser beam. The list of disappointing crystals will not be given here. On the positive side, one very interesting compound was turned up, 4-amino-4'-nitrodiphenyl sulfide (ANDS). This compound was the first that had been investigated to contain sulfur as the electron donor. It had a harmonic generating efficiency comparable to the best known organic materials, most of which contain amine groups as donors. Furthermore, ANDS itself held promise for device application; its powder response vs particle size demonstrated that its birefringence was sufficient for phase matching at the YAG frequencies. Attention was thus given to the determination of its crystal structure. This latter showed that the molecular orientation in the crystal is determined largely by significant amino-nitro interaction through hydrogen bonding, and the expected, high components of the β tensor are very favorably aligned for contribution to the $\chi^{(2)}$ tensor. This study forms the next section of this Report. ANDS thus was to serve as a foot-in-the-door prototype for broadening the investigation to derivatives and other chalcogen analogues.

During the second year organic synthesis got under way as did the EFISH measurements. Below in sections IV and V, we discuss the EFISH measurements and the synthetic work.

III. A. SHG Experiment on ANDS

The experimental apparatus consists of a Quantel International Q-switched Nd:YAG laser, series YG580. The laser has an output energy of approximately 0.9 J/pulse at 1.064μm with a width of 15 nsec, and a repetition rate of 10 Hz. The laser beam was split into two halves, one was sent to the reference cell, which contained urea, the other was sent to the sample cell. Both cells are made of quartz and have known thickness. Neutral density filters were used to control the intensity of the incident beam, and narrow band pass filters were used to insure that only the 1.06μm radiation reaches the sample and only the 0.532μm light reaches the detectors. An RCA 2022 phototube with an S-1 surface was used to detect the second harmonic light.

The sample was purified by vacuum sublimation, then sieve-graded to different particle sizes ranging from 25-212μm. Purity analysis via DSC was not possible owing to the thermal decomposition of the compound near its melting point. The efficiency of the sample for SHG was measured at different particle sizes and compared to that of urea at the same particle sizes and cell thickness.

Figure 1 shows the dependence of SHG efficiency (in arbitrary intensity units) as a function of particle size. The levelling off of the curve at large sizes demonstrates that the crystalline material is phase matchable at the wavelengths used.[2] While it is not possible to make quantitative comparisons using the powder method, the values given in Table I suggest that ANDS is in a class with some of the best studied nonlinear optical materials.

Table I

Organic Compounds with Large Second Order Susceptibilities

Compound[a]	Relative SHG Intensity[b]	Reference[c]
KDP	0.3	
Urea	1	
ANDS	20	
MNA	22	9,10
POM	13	11,12
MAP	10	13
NPP	50	14

a. Structures are shown in the accompanying scheme below. b. Determined by the Kurtz and Perry[2] powder method. For a more extensive comparison of organic compounds see reference 35a. c. These have all been checked in our laboratory.

The visible absorption spectrum is given in Fig. 2. It is seen that absorption of the second harmonic at 532 nm is not appreciable, but the material would not be useful for doubling frequencies much higher than that of the Nd:YAG fundamental, a limitation shared with the analogous compounds of the preceding paragraph.

III. B. Structure Determination

Crystals of 4-amino-4'-nitrodiphenylsulfide were grown by vapor diffusion in a large sublimator. At a pressure of approximately 50 millitorr and a

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temperature of 115-118°C, yellow, needle-shaped crystals formed on top of the crude material. A crystal of dimensions 0.3 x 0.25x 0.25mm^3, mounted with the needle (c) axis approximately along the goniometer ϕ axis, was used for data collection. Unit cell constants, a = 6.688(4), b = 7.367(3), c = 23.380(7), were determined by least squares fit to the setting angles of 24 reflections in the range 32°<2θ<54°. Based on a unit cell volume of 1152 A^3, Z=4, and molecular formula $C_{12}H_{10}N_2O_2S$, calculated density ρ_{calc} = 1.42g/cm^3. Measured density ρ_{obs} was 1.42(1) g/cm^3.

Data were collected at room temperature using the ω -θ scan technique with a scan rate varying between 2° and 20°/min, and CuK_α radiation on an ENRAF-NONIUS CAD-4 diffractometer.[15] Maximum 2θ for collected data was 150°. Systematic absences of hkl, h + k odd and h0l, l odd were consistent with the acentric space groups $Cmc2_1$ and C2cm. Absence of centrosymmetry had been proven from observed nonlinear optical properties. The 1505 reflections collected yielded 517 unique nonzero data. Lorentz and polarization corrections were applied; no absorption correction was attempted (μ = 23.6 cm^{-1} for CuKα).

Space group $Cmc2_1$ was initially assumed for the structure solution (based on packing considerations), and confirmed by success of refinement. The structure was solved by standard Patterson and Fourier techniques, and refined by least squares. As the refinement progressed, it was noted that the fit of F_{obs} to F_{calc} for the 200 reflection was very poor ($\Delta F > 5\sigma$); this reflection was then given a zero weight in least squares (but included in Fourier calculations). The final R value was 8.2%, weighted R was 8.1% and goodness of fit was 2.05.[16] The largest peaks in a final difference Fourier map were about 0.3 $|e|/A^3$, in the vicinity of the sulfur atom.

Thermal parameters resulting from refinement are anomalously large, most notably B_{11} for atoms in or near the amino- and nitro- groups. Since the model constrains all of these atoms to lie on a crystallographic mirror plane, these thermal parameters may signal some disorder. Orientational disorder of the nitro- group seems most likely, as aromatic nitro compounds most often show some tipping or tilting of the nitro plane away from the plane of the aromatic ring, for steric reasons.

An 010 projection of the unit cell contents is shown in Figure 3. The molecules pack in a herringbone-like array, with the long molecular dimension in the c-direction and the molecules located on a mirror plane perpendicular to a. The nitro substituted phenyl ring lies in this mirror plane, while the amino-substituted ring lies (exactly) perpendicular to this plane. Bond lengths and angles are given in Figure 4; the standard deviation for bond lengths is .01A and that for bond angles is 1 degree unless otherwise noted.

The molecular geometry of 4-amino-4'-nitrodiphenylsulfide shows no particular surprises: the 104° bond angle at the sulfur is near the tetrahedral angle and, except for the 1.42 Å C11-C12 bond, the bond lengths and angles are consistent with those generally observed. The exactly perpendicular orientation of the phenyl rings might not be expected; structures of similar diphenylsufides show no preferred orientation of these rings.[17] This and the bond angle at the sulfur indicate that conjugation between the rings is absent.

The C6-N7 (amino) bond length of 1.45(1) Å is notably (almost 0.1Å) longer than aromatic C-N(amino) bond lengths are generally observed to be. The 1.49(1)Å C14-N(nitro) bond lengths is at the high end of the range observed for aromatic nitro groups.[18].

There are a few notable intermolecular contacts, the most outstanding of which consists of a close approach between the amine end of one molecule (x,y,z) and the nitro end of a neighboring one (x,1-y,1/2+z). This is suggestive of hydrogen bonding, which offers a reasonable explanation of why this achiral and dipolar molecule would choose to form a noncentrosymmetric crystal structure. The N(amino)-O(nitro) distance is 2.97Å, and the orientation is one which would bring the amine hydrogens quite close to that oxygen. The disorder mentioned above makes any attempt to quantify N-H-O contacts questionable .

There are also close contacts involving atoms in each of the phenyl rings: C3(x,y,z)--C4(1/2-x,1/2+y,z) at a distance 3.37Å (the sum of the van der Waals radii is 3.5Å), and C12(x,y,z)--C15(1/2+x,1/2+y,z) with a distance of 3.51Å. There is also a close approach between S(z,y,z) and C16(1/2+x,-1/2+y,z) at 3.67Å, only slightly greater than the relevant sum of van der Waals radii (3.6Å). All of these contacts occur between molecules related as a whole by the lattice centering operation.

The overall picture of the crystal structure of ANDS shows molecules linked by hydrogen bonding in the c-direction, and by close approaches of phenyl rings in the 110 direction.

III. C. Discussion

The structure of the molecule itself in the crystal is interesting in that not only is the bond at the sulfur almost exactly tetrahedral but the planes of the two rings are rigorously mutually perpendicular. This rules out any contribution to optical nonlinearity by charge transfer interaction between the $-NH_2$ and the $-NO_2$ moieties.[19] Thus, the contributing charge transfer directions are either $NH_2 \rightarrow S$ or $S \rightarrow NO_2$. In order to obtain a preliminary idea of the electronic structure of ANDS, a CNDO approximate molecular orbital

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calculation was carried out on the molecule using the geometry obtained from the crystal structure study. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are both of pi-symmetry with respect to the $S-Ph-NO_2$ plane, and show little contribution from the H_2N-Ph side of the molecule. The pi molecular orbital coefficients for the HOMO and LUMO are shown in Figure 5, where the size of the circles for each atom is proportional to the coefficient for the p_π basis function centered on that atom. The HOMO is predominantly of sulfur p character while the LUMO includes significant contribution from the nitrophenyl group. Thus a HOMO $\rightarrow$ LUMO excitation should correspond to a sulfur to ring and nitro group transition. The small asymmetry noted in the orbital coefficients is a result of using the observed bond lengths and angles rather than using an idealized geometry. As noted earlier, there is a clear indication of a hydrogen bond between one amine hydrogen and one nitro oxygen. This holds the molecules in a head-to-tail arrangement that is beneficial in providing constructive summation of the molecular hyperpolarizability β to the macroscopic second order electric susceptibility $\chi^{(2)}$. Purely electrostatic, dipolar interactions tend to favor opposing moments, which often results in centrosymmetric crystal point groups. The latter demands total cancellation of the β's and the vanishing of $\chi^{(2)}$.

Although centrosymmetry is the rigorous requirement for total cancellation of all molecular β components, non-rigorous, partial cancellation is generally the rule for non-centrosymmetric crystal point groups. The ability of the components of β to be reflected in the components of $\chi^{(2)}$ depends upon the orientation of the molecules in the unit cell. Zyss and Oudar[20] have considered this question in detail for cases in which the molecular β tensors are either "one" or "two-dimensional", that is, whether the β tensor has the shape of a cigar or a crêpe, respectively.

For molecules in which the high hyperpolarizability is confined to the direction of charge transfer between two groups through π-conjugation, the β tensor is one-dimensional to a very good approximation. A thorough, theoretical investigation of para-nitroaniline by Lalama and Garito[21] has definitively shown this to be true. The component β_{xxx} (x being the charge transfer axis) contributes about 90% to the χ component of the "vector part" of the β tensor.[22] The similarity between para-nitroaniline and the "active"

-S-   -NO$_2$ moiety of ANDS should qualify this molecule as a one-dimensional example.

The requirements for phase matching demand more than a simple alignment in the crystal of these one-dimensional entities. The ability to use the crystal's birefringence to match the phase velocity of the fundamental wave and the harmonic (in the case of SHG) is far more important from a practical point of view [28,29] than is a large value of $\chi^{(2)}$. Of the three waves mixing in the crystal, two are at frequency ω and one is at 2ω. Furthermore, for non-critical phase matching[30] to which Zyss and Oudar[20] necessarily limit their discussion for the sake of fixing the laser beam to the crystal axes directions, the polarization vectors $\vec{e}_\omega$ and $\vec{e}_{2\omega}$ are mutually perpendicular. It is physically obvious that, for maximum polarization of the medium, the plane of these vectors should contain the microscopic vector $\vec{\beta}_{1d}$ (the one-dimensional molecular tensor). Thus, the most favorable angle θ between $\vec{\beta}_{1d}$ and the pair of unit polarization vectors $\vec{e}_\omega$ and $\vec{e}_{2\omega}$ will be given by maximization of the projection function $\sin\theta \cos^2\theta$, if θ is measured from $\vec{e}_\omega$.

This yields $\theta_{opt} = 35.26°$.

Zyss and Oudar[20] have discussed this optimization of molecular alignment for one-dimensional molecules in all of the crystal point groups for non-critical, type I phase matching, assuming that one molecule occupies a general position within the unit cell. In nature it would be unlikely to find a compound which cooperated by satisfying these stringent conditions, but θ_{opt} does provide a guide; clearly, if $\theta = 0$ or $\pi/2$ there would be no contribution of β_{1d} to $\chi^{(2)}$.

For the point group $D_{2h} = mm2$ of ANDS, two pairs of molecules, related by m, Fig. 6, are generated by the symmetry elements. All four can contribute optimally to the nonlinear interaction if the molecules of each pair are inclined at an angle of 35.26° from the two-fold axis. With axes labelled as in Fig. 6 the laser beam ω would enter along the X axis polarized in the Y direction and the harmonic 2ω would emerge polarized in the Z direction. Actually the angle θ is 40° for this crystal. Thus, the nonlinear interaction should be 93% of the optimum!

IV. Electric Field Induced Second Harmonic Generation - EFISH

As pointed out in the above Review of the Theory section this measurement on polar molecules yields the projection of the "vector part" of the β tensor on the dipole moment direction. The vector part, for μ chosen to be the x molecular direction, would be

$$\beta = 1/3(\beta_{xxx} + \beta_{xyy} + \beta_{xzz} + 2\beta_{yyx} + 2\beta_{zzx}).$$

It is seen that although only one number is determined, it can reflect the magnitude of the largest β components provided that large β components are aligned with the electric moment. One would expect this to be the usual case since charge transfer directions as well as dipole moment directions often point across a molecule from donor to acceptor functional groups. The mole-

cules to be measured in solution must be partially aligned by an electric field pulsed and synchronized with the laser pulse. In the setup assembled here the timing is obtained from the 24 volt pulse of a Quantel International Model 581 Nd:YAG oscillator. This pulse starts the charging of the flashlamp capacitors and triggers a delay generator. The latter tips off the square wave field pulse generator that the Q-switching of the YAG rods is about to take place. The field then turns on for about five microseconds so that by the time the 10 ns, 1.064µm fundamental laser pulse arrives it sees a D.C. field in the sample. The field electrodes and cell windows are designed for field homogeneity within the liquid being measured. The windows are maintained at an angle of ca. 1° from each other so that the sample is confined in a wedged cavity which, when translated by a precision stage perpendicular to the laser beam, slowly increases or decreases the path length. As this change occurs, interference effects in the generated harmonic wave produce fringes that can be measured to yield the refractive index difference $n_{2\omega} - n_\omega$ needed for the calculation of β.

The fundamental laser beam is split. The leg that does not go to the sample is sent through a quartz plate to generate harmonic intensity that can be compared with that in the sample. These two beams are filtered to remove fundamental and are then detected by identical type 8850 RCA photomultipliers. The output of the PMT's is fed to an EGG/PAR Series 4400 data processor in which each data point is usually averaged for 32 shots. About 500 of these points are stored for the sample and quartz reference curves and, at the end, the former is divided by the latter to attempt to compensate for intensity wandering of the laser output. The resulting curve can also be smoothed for easier measurement of the fringe spacing, or otherwise treated in the processor. The translating stage is then set for a maxi-

sum in the sinusoidal fringe curve and averaged for another 16,000 pulses. This number gives the harmonic generating power of that solution relative to a wedged quartz plate which stands on the same stage and which is moved into the beam by further translation. The samples are always run at several concentrations and the relative intensity is plotted vs concentration in order to assess the quality of the data and to remove the contribution of the solvent by extrapolation to infinite dilution. Refractive indices are measured with a hollow prism and a HeNe Laser, then extrapolated to $2\omega = 532$ nm.

Results to date are reported in Table II. Measurements have been made on the compounds
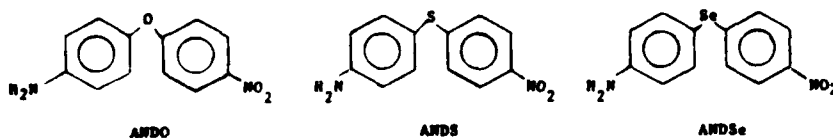
to determine the effect of replacing the chalcogen. These have been done in polar and non-polar solvents. Another class of compounds was started
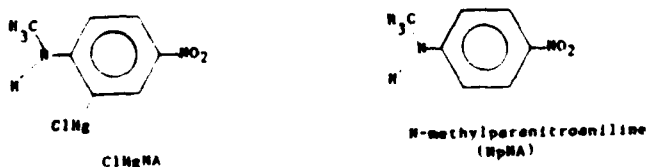
because the mercurated compound was found to give a very high response as a powder. Paranitroaniline was run as a test for comparison with the extremely careful study of this molecule by Garito's group.[31] The solvents used do not give a strong signal when pure and so their contributions Γ_1 were difficult to assess in that way. Nevertheless the Γ_1 (meas.) column in Table II lists the results of such attempts. The Γ_1 (extrap.) column gives more precise values of Γ_1 obtained by our extrapolation procedure to infinite dilution. These two columns should, of course, agree and are seen to be quite

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Table II

Solvent Effects and Hyperpolarizabilities of Some Related Molecules

Solute	Solvent	$\Gamma_1 \times 10^{14}$ esu (extrap.)	$\Gamma_1 \times 10^{14}$ esu (meas.)	$\mu\beta \times 10^{46}$ esu	$\beta \times 10^{29}$ esu
ANDS - Powder, 21[†]					
	Benzene	7.5	0	1.27	3.1
	Dioxane	4.6	4.75	1.43	3.5
	Methanol	6.2	5.5	1.68	4.1
	Acetone	7.65	7.5	1.53	3.75
ANDO - Powder, 0					
	Dioxane	5.2	4.75	1.32	3.5
	Methanol	5.7	5.5	1.63	4.3
ANDSe - Powder, 14					
	Dioxane	4.45	4.75	1.40	3.5
pNA - Powder, 0					
	Dioxane	4.6	4.75	1.17	1.71[*]
N-Me-pNA - Powder, 0.3					
	Acetone	7.8	7.5	2.12	3.0
N-Me-pNA-HgCl - Powder, 21					
	Acetone	7.7	7.5	1.88	3.55

[†]Powder data are normalized to the response of urea, all with 0.1 mm path length.

[*]Compare to 1.69 ± 0.04 of reference 31.

close. What was done for Γ_1 (extrap) was the following: the calculation of the solute's β was run through and plotted <u>vs</u> concentration for different estimates of Γ_1. Since none of the quantities in the calculation should change sharply with concentration as it approached zero, we chose that value of Γ_1, which gave a straight line for the β <u>vs</u> conc. curve. For a choice of Γ_1 too high, too little contribution was left for attribution to the solute, and the β curve turned downward; for Γ_1 too low the opposite occurred. These deviations at low concentration appeared to be quite abrupt, providing a very sensitive and simple choice of the best Γ_1. The next column $\mu\beta$ lists that product, because this was measured to better precision than μ itself. The dipole moments have not at this time been carefully determined in different solvents due to the lack of the appropriate equipment. However, using roughly measured and estimated μ's, we arrive at the values of β listed in the last column. These values are believed to be accurate to $\pm 5\%$.

The first observation that is somewhat surprising is that the values of β are all about the same and that the large harmonic conversion efficiencies of the mercury compound and of ANDS compared to their relatives must be seated in the crystal structure and not the molecular hyperpolarizabilities. It would indeed be interesting to have a structure determination of the crystalline mercury derivative.   Another unexpected result is the lack of a solvent effect.   Paranitroaniline, for which there is a striking solvent effect between methanol[32] and dioxane[31] was run in order to see if the previous determinations could be repeated.   The dioxane result was, duplicated precisely as can be seen in Table II, and so was the methanol. However the latter has not been included because the quality of the methanol data is lower than that of the rest of the table. Recent work[33] has shown the importance

of the lower electronic excited states. One would thus expect that compounds whose electronic spectra exhibited marked solvatochroism would be the ones whose β's were substantially solvent dependent. Our vis-uv spectra of the ANDS family are not greatly dependent upon solvent polarity; the converse is true for paranitroaniline. The behavior of N-methyl-4-nitroaniline in comparison with its mercuriated analogue is truly remarkable. Although molecular hyperpolarizability and crystalline bulk response are known to be only remotely related, so much depending upon molecular orientation and crystal symmetry, we did expect more of a difference between their β values than is seen in Table II. The interesting questions raised are: does the chloromercury appendage simply nudge the organic moiety into an orientation which takes advantage of its modest hyperpolarizability or is the hyperpolarizability at the molecular level greatly enhanced through intermolecular interaction involving the metal atoms?

Another comment should be made on these data. There is a striking discrepancy for the solvent Γ_1 for ANDS in benzene between the response measurable for pure benzene, zero, and the value obtained by extrapolation of the solutions' response to infinite dilution, 7.5×10^{-14}. No explanation for this is available. It may signal a specific interaction between the solute and solvent; this would not be unexpected for the case of benzene, the only solvent used that has a π electron system. It would indeed by interesting to obtain more data on this and related systems.

We find it interesting that in some cases, but not all, there is a marked dependence of β upon concentration, which was unexpected for concentrations approaching zero. The slope can be positive or negative and depends upon both solute and solvent. Insufficient data have been assembled to suggest an explanation at this time, but the results are displayed in Table III.

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TABLE III.

Slope of β vs Active Molecules per Cubic Centimeter

at Infinite Dilution

Active Molecule	Solvent	Slope x 10^{50} esu/conc. unit
p-nitroaniline (pNA)	dioxane	0
N-methyl pNA	acetone	+18
N-methyl pNA-HgCl	acetone	+30
ANDO	methanol	0
ANDO	dioxane	-42
ANDS	methanol	0
ANDS	dioxane	0
ANDS	acetone	-9
ANDS	benzene	-14
ANDSe	dioxane	-17

V. Synthesis and Nonlinear Optical Properties of Some Substituted Ruthenium(II) η^5-Cyclopentadienyl η^6-Arene Salts.

Although a large number of inorganic and organic compounds have been tested for their efficiency as frequency doubling media, organometallic compounds are a class of materials that have not been examined in any depth.[34] A cursory survey of these compounds would initially suggest that this should not be a good group of materials to study because of the low energy d-d transitions that gives rise to the so-called "transparency-efficiency trade-off." For a substance to be used in a frequency doubling capa-

city, it must not absorb the harmonic light that is produced. Certainly absorption of visible light would limit the useful frequency doubling capability of these materials. However, the attractive feature of this group is the rather polarizable extended π-electron network of the ligands which in conjugation with the d-electrons of a transition metal could give rise to useful nonlinear optical properties. Previous research on nonlinear optical properties of organic compounds has shown that an intramolcular donor-acceptor combination which allows for a large charge-transfer transition, such as occurs in p-nitroaniline, is a primary factor in producing materials with desirable nonlinear optical properties.[35]

Reported herein is the synthesis and preliminary nonlinear optical study of several new arene-Cp-ruthenium complexes (Cp = η^5-C_5H_5). In three of these organometallic ruthenium compounds, p-nitroaniline derivatives were used as ligands in an effort to increase the molecular hyperpolarizability of the compounds.

Results and Discussion

There are three general procedures for preparing arene-Cp-ruthenium complexes. Nesmeyanov and co-workers[36] reported the synthesis of ruthenium complexes by exchanging one Cp ligand of ruthenocene for various arenes. Zelonica and Baird[37] showed that the chlorines in the dimeric complex, [(η^6-C_6H_6)RuCl$_2$]$_2$, are readily substituted via thallium cyclopentadienide in acetonitrile thus producing [(η^6-C_6H_6)Ru(η^5-C_5H_5)]Cl in good yield. Recently, Spies and Angelica[38] have developed a new and very convenient route leading to [(η^5-C_4H_4S)Ru(η^5-C_5H_5)]BF$_4$ **2**. This method involves refluxing, under N$_2$, (η^5-C_5H_5)Ru(PPh$_3$)$_2$Cl **1**, thiophene and AgBF$_4$ in absolute methanol for 72 h. We chose this last procedure since it could provide arene-Cp-ruthenium complexes with nitro- (electron acceptor) and amino- or N,N-disubstituted amino- (elect-

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ron donor) substituents in the arene ligand. However, we have found that stirring the reaction mixture for 24 h at 25° C under Ar gave better yields than refluxing the solution 3 days under N_2. A sample procedure is as follows: $[(\eta^5-C_5H_5)Ru(PPh_3)_2]Cl$ **1**, $AgBF_4$, and nitrobenzene, in absolute methanol, were stirred for 24 h at 25° C, the solvent was removed in vacuo and the residue was extracted with methylene chloride. The product, $[(\eta^6-NO_2C_6H_5)Ru(\eta^5-C_5H_5)]BF_4$ **3**, was crystallized with diethyl ether (60% yield). The IR spectrum exhibits absorption bands at 1350 and 1560 cm^{-1} ($-NO_2$), and 1000 ~ 1150 cm^{-1} (BF_4^-). The ^1H NMR spectrum shows a singlet at δ 5.50 (Cp) and multiplets centered at δ 6.45 (3H, aromatic protons) and 7.15 (2H, aromatic protons adjacent to $-NO_2$). Compounds **4, 5,** and **6** were obtained in a similar fashion, except that p-nitroaniline derivatives (N,N-dimethyl-4-nitro-aniline = FMNA, 2-methyl-4-nitroaniline = MNA, or (S)(-)-2-hydroxymethyl-1-(4-nitrophenyl)-pyrrolidine (NPP)) were used in the place of nitrobenzene. These reactions are depicted in Scheme 1. The crystalline ruthenium complexes (**2, 3, 4, 5,** and **6**) are stable in air and are soluble in methylene chloride and acetonitrile. Solutions of these complexes are somewhat air sensitive and showed gradual decomposition after several days.

A comparison of the ^1H NMR spectra of compounds **3, 4, 5,** and **6** shows that the influence of the amino-donor group on the chemical shift of the Cp-ligand protons is between 0.1 and 0.2 ppm. See Table IV. The increased conjugation of the p-nitroaniline ligands causes a shielding effect on the Cp resonances. In the case of an MNA ligand, the influence is smaller than the others because of steric inhibition of resonance resulting from the o-methyl group. The IR spectra of these complexes are consistent with the presence of the $-NO_2$ group, with bands at 1350 and 1550 cm^{-1}, and BF_4^- between 1000 ~ 1300 cm^{-1}. The UV-VIS spectra of **4, 5,** and **6** basically show two large absorptions

Scheme 1

RuCl$_3$

i,ii

O_2N— (ring) —N (pyrrolidine) $^{7+}$
HO— * BF$_4^-$

6

$^{7+}$
S— (ring)
Ru BF$_4^-$

2

NPP
iii
Ph$_3$P—Ru—Cl
PPh$_3$
1

TP
iii

MNA
iii

NB
iii

iii DMA

O_2N— (ring) —NH$_2$ $^{7+}$
Ru BF$_4^-$

5

(ring) —NO$_2$ $^{7+}$
Ru BF$_4^-$

3

O_2N— (ring) —N(CH$_3$)$_2$ $^{7+}$
Ru BF$_4^-$

4

i= (cyclopentadiene) , ii= PPh$_3$,

iii= AgBF$_4$

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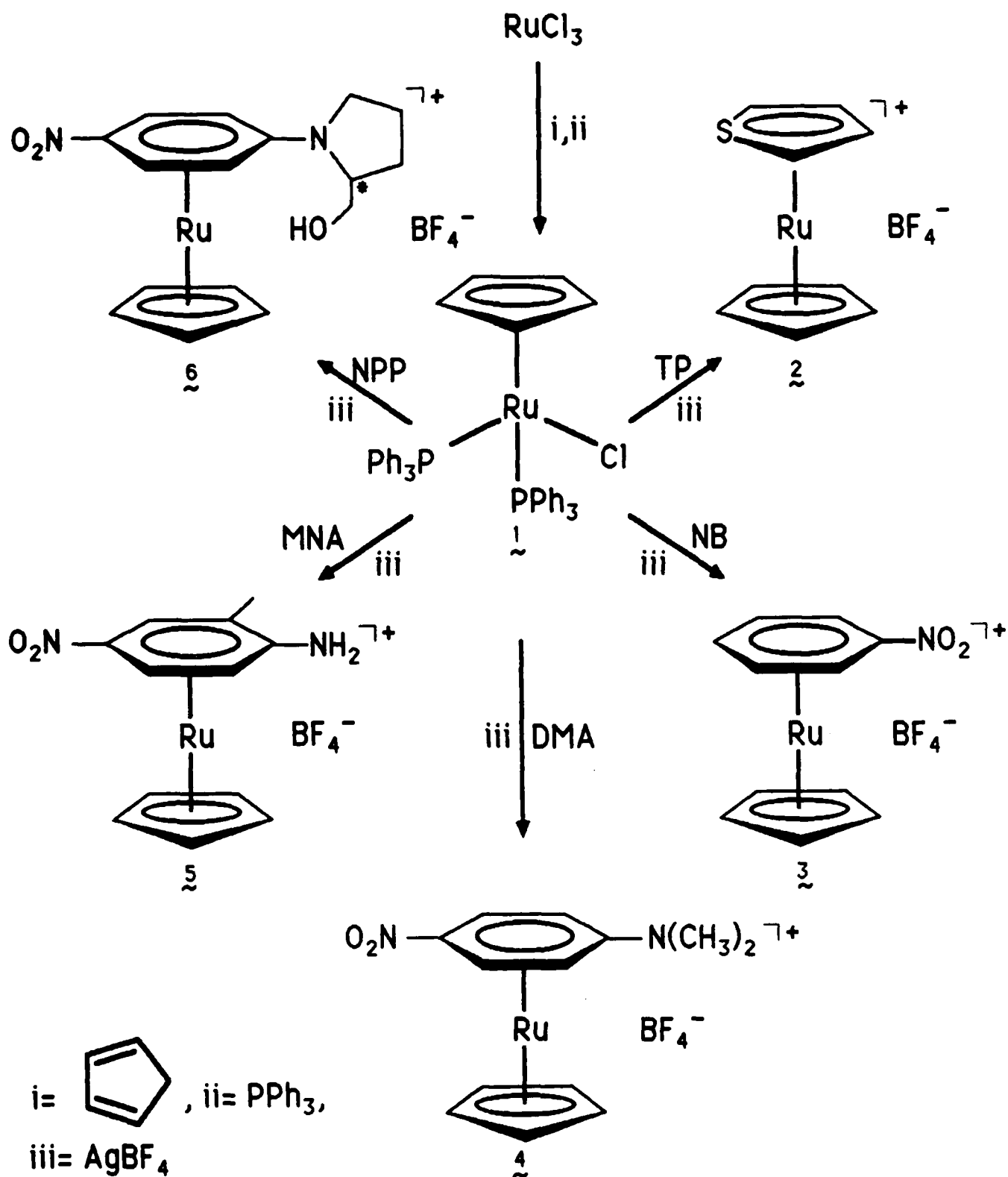
TABLE IV.

^{1}H NMR Spectra of $[(\eta^{6}\text{-arene})Ru(\eta^{5}\text{-}C_5H_5)]BF_4$*

Ruthenium Complex	Arene, ppm	C_5H_5, ppm
2	6.50(m, 2H), 6.57(m, 2H)	5.49(s, 5H)
3	6.45(m, 3H), 7.15(m, 2H)	5.50(s, 5H)
4	5.65(d, 2H), 6.90(d, 2H)	5.30(s, 5H)
5	6.35(d, 1H), 7.05(d, 1H), 7.20(s, 1H)	5.40(s, 5H)
6	5.86(d, 1H), 5.95(d, 1H), 6.90(d, 2H)	5.40(s, 5H)

*s = singlet; d = doublet; m = multiplet; signal intensity is also given in parentheses.

in the UV region. The UV absorptions, at longer wavelengths, are 291 (log ε = 3.91), 276 (3.80), and 300 nm (3.93), for 4, 5 and 6, respectively. The pattern of the UV spectrum of 3, however, is quite different from the others exhibiting only weak d-d absorptions between 300 and 500 nm. That is, there is no band due to a charge-transfer transition. As all of the p-nitroaniline ligands used here display an intense charge-transfer absorption band in the near ultraviolet region, it is noteworthy that the UV absorptions of the ruthenium complexes with the p-nitroaniline derivatives as ligands show charge-transfer absorptions which are blue shifted. This trend is illustrated in Figs. 7 and 8 where the electronic spectrum of the free ligand NPP is compared with that of the corresponding ruthenium complex. In terms of practical laser frequency doubling the absorption edge should be near the wavelength of the second harmonic but not include it as was noted for these compounds when 1064 nm radiation is used.

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The relative efficiency of second-harmonic generation[39] (SHG) for these compounds are summarized in Table V. The SHG efficiency of each ruthenium complex is on the order of urea but is substantially lower than the best organic compounds (e.g., NPP is 50 × urea). We also measured the SHG efficiency of $[(\eta^5\text{-dienyl})Ru(\eta^6\text{-arene})]X$ listed in Reference 40, and again observed similar efficiencies (0.7 ˜ 1.0 relative to that of urea). All of the

TABLE V.

Second Harmonic Intensity for a Series of Powders[a]

Compound	Relative Second Harmonic Intensity[b]
Urea	1.0
1	0.7
2	0.7
3	0.7
4	0.9
5	1.0
6	0.7

[a]The fundamental radiation is supplied by a Quantel International Q-Switched Nd:YAG laser, with about 0.9 J/pulse at 1064 nm and with a repetition rate of 10 Hz, and a pulse width of 15 ns. [b]Relative to SHG intensity of urea.

ruthenium complexes studied decomposed to some extent in the radiation field (1064 nm) generated by Nd:Yag laser source (0.9 J/pulse).

The lower than hoped for SHG efficiency could be the result of either a molecular or crystal structure problem as discussed in a previous section.

Experimental

Melting points were determined in sealed capillaries on a Thomas-Hoover Unimelt melting point apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer 347 IR spectrophotometer. UV-Visible spectra were taken in CH_3OH on a Varian-Cary 219 spectrometer. ^1H NMR spectra were recorded at 80 MHz, in CD_3CN or acetone-d_6 on a Varian CFT-20 spectrometer. Chemical shifts are reported in ppm downfield from an internal standard, tetramethyl-silane. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. (s)(-)-2-Hydroxymethyl-1-(4-nitrophenyl)pyrrolidine or N-(4-nitrophenyl)-(L)-prolinol (NPP) was prepared according to a published procedure.[41] For the SHG studies the instrumentation and procedure was the same as that described in a previous publication.[39]

[(η^5-Thiophene)Ru(η^5-C_5H_5)]BF$_4$ (2).[38]

A solution of [(η-C_5H_5)Ru(PPh$_3$)$_2$]Cl (1)[42] (1.00 g, 1.38 mmol) in thiophene (12 mL) was added to a suspension of AgBF$_4$ (0.35 g, 1.80 mmol) in absolute methanol (10 mL) and thiophene (7 mL), and the mixture was stirred under Ar at 25° C for 24 h. The solvents were evaporated in vacuo, the residue was taken up in methylene chloride (20 mL) and filtered to remove AgCl. Addition of diethyl ether (20 mL) to the filtrate gave 2 (242 mg, 73%) as a white solid: mp 295° C (dec); ^1H NMR (acetone-d_6) δ 5.49 (s, 5H, C_5H_5), 6.50 (m, 2H, thiophene H (2,5)), 6.57 (m, 2H, thiophene H (3,4)).

[(η^6-nitrobenzene)Ru(η^5-C_5H_5)]BF$_4$ (3).

A solution of 1 (1.00 g, 1.38 mmol) in nitrobenzene (20 mL) was added to a suspension of AgBF$_4$ (0.30 g, 1.54 mmol) in absolute methanol (10 mL) and the

mixture was stirred under argon at 25° C for 24 h. After filtration of AgCl, addition of diethyl ether (150 mL) to the filtrate gave a pale brownish-yellow solid. The solid was then dissolved in acetone (5 mL) and slow addition of diethyl ether (50 mL) gave **3** as pale yellow crystals in 47% yield: mp 308 ˜ 312° C (dec); UV (methanol) 312 nm (log ε = 3.04), 368 (2.81), 410 (2.59), 470 (2.24), and 500 (2.12); IR (KBr) 3045, 3030, 3000, 2950, 2900, 2820, 1560, 1350, 1150-1000 (BF_4^-), 855, 845, 682 cm^{-1}; ^1H NMR (CD_3CN) 5.50 (s, 5H, C_5H_5), 6.45 (m, 3H, nitrobenzene 3, 4, 5) and 7.15 ppm (m, 2H, nitrobenzene (2,6)); Anal. Calcd. for $C_{11}H_{10}BF_4NO_2Ru$: C, 35.12; H, 2.68; N, 3.72. Found: C, 35.17; H, 2.69; N, 3.73.

[η^6N,N-Dimethyl-4-Nitroaniline)Ru(η^5-C_5H_5)BF$_4$ 4.

A solution of **1** (1.00 g, 1.38 mmol) and N,N-dimethyl-4-nitroaniline (3 g, 18 mmol) in methylene chloride (140 mL) was added to a suspension of $AgBF_4$ (0.3 g, 1.54 mmol) in absolute methanol (10 mL) and the mixture was stirred under argon at 25° C for 24 h. After the filtration of AgCl, addition of diethyl ether (150 mL) to the filtrate gave a brownish-yellow solid. The solid was then dissolved in acetonitrile (10 mL) and slow addition of diethyl ether (50 mL) gave **4** (310 mg, 62%) as a yellow solid; **4** mp 282-285° C; UV (methanol) 216 nm (log ε = 4.35), 270 (3.94), and 294 (3.91); IR (KBr) 3105, 2900, 2820, 1560, 1350, 1080 ˜ 1040 (BF_4^-), 750, 650, 610 cm^{-1}; ^1H NMR (CD_3CN) δ 2.85 (s, 6H, methyl), 5.30 (s, 5H, C_5H_5), 5.65 (d, 2H, J = 9 Hz), and 6.90 (d, 2H, J = 9 Hz); Anal. Calcd. for $C_{13}H_{15}BF_4N_2O_3Ru$: C, 37.25; H, 3.61; N, 6.68. Found: C, 37.16; H, 3.63; N, 6.62.

[(η^6-2-Methyl-4-nitroaniline)Ru(η^5-C_5H_5)]BF$_4$ 5.

Compound **5** was prepared in an analogous manner using 2-methyl-4-nitroaniline (MNA) (2.25 g, 14.8 mmol). Yield 310 mg, 55.5%: mp 185-187° C; UV (methanol) 206 nm (log ε = 4.29), 244 (3.82), 276 (3.80); IR (KBr) 3450, 3360,

3250, 3090, 2900, 1640, 1560, and 1350 (NO_2), 1000 ‾ 1100 (BF_4^-), 850, 820,

760, and 670 cm^{-1}; ^1H NMR (acetone-d_6) 2.50 (s, 3H, methyl), 2.81 (s, 2H,

NH_2), 5.40 (s, 5H, C_5H_5), 6.35 (d, 1H, J = 8 Hz), 7.05 (d, 1H, J = 8 Hz), and

7.20 (1H, s). Anal. Calcd. for $C_{12}H_{13}BF_4N_2O_2Ru$: C, 35.58; H, 3.28; N, 6.92.

Found: C, 35.85; H, 3.49; N, 6.73.

$[(\eta^6$-N-(4-Nitrophenyl)-(L)-prolinol)Ru(η^5-C_5H_5)]BF_4 6.

Complex 6 was prepared in an analogous manner using N-(4-nitrophenyl)-

(L)-prolinol (2.7 g, 12.2 mmol). Yield 330 mg, 50.3%: mp 192-195° C; UV

methanol 217 nm (log ϵ = 4.30), 276 (3.93), and 300 (3.93); IR (KBr) 3560,

3300, 2920, 2870, 1550, and 1340 (-NO_2), 1010 ‾ 1100 (BF_4^-), and 650 cm^{-1}; ^1H

NMR (CD_3CN) 2.70 ‾ 4.00 (m, 10H), 5.30 (s, 5H, C_5H_5), 5.86 (d, 1H, J = 7.2

Hz), 5.92 (d, 1H, J = 7.2 Hz), and 6.9 (d, 2H, J = 7.2 Hz); Anal. Calcd. for

$C_{16}H_{18}BF_4N_2O_3Ru$: C, 40.53; H, 3.83; N, 5.91. Found: C, 40.37; H, 4.18; N,

5.76.

VI. Conclusions

Of the molecules measured with EFISH there is a striking constancy of

their $\mu\beta$ products and even the more approximate β's themselves. This is not a

general finding, as β's have been found to vary over several orders of magni-

tude for different classes of compounds.[43] These molecules are all nitro-

benzene derivatives and the observation could be made that the magnitude of β

is more or less tied to this conjugated portion of the molecules. Comparison

of the powder data with the molecular hyperpolarizabilities illustrates a

principle which is not appreciated even in the most modern literature, that

is, that a study of powder response tells essentially nothing whatever about

molecular properties. Too much depends upon the crystal structure. It is to

this latter property that attention should be directed in the search for

materials destined for application to the processing of weak optical

signals.

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Solvent affects show a qualitative increase of $\mu\beta$ with solvent polarity. This has been seen before in the few cases studied.[31,32] Not enough has been done to warrant quantitative comparisons. Influence of hydrogen bonding between solute and solvent is not, as yet, separable from polar effects. Accurate electric dipole moment data are necessary for quantitative interpretation, but the fact that the solvent has little influence on β is apparent and is consistent with the immutability of the lowest electronic absorption bands. The lowest band of ANDS shifts only some 80 cm^{-1} between methanol and dioxane while the shift is 1300 cm^{-1} for the analogous band of pNA.

The dependence of β (or $\mu\beta$) on concentration in some solvents for some solutes at very low concentrations is interesting and has not been clearly seen before. These measurements were all made on solutions of less than 1 molecular percent and so solute-solute interaction almost certainly is absent. This definitely demands more work, as it bears directly on theories of solution.

The process of surveying a large number of powdered solids for SHG efficiency is inefficient, a conclusion exemplified by this research and by others.[2,12] Two compounds, ANDS and ClHgNA have emerged as winners, but the work slowed before crystal growing attempts produced large crystals of the right shape for craftwork. Measurements made on some newly synthesized ruthenium (II) η^5-cyclopentadienyl η^6-arene salts as powders demonstrated a rather low frequency doubling efficiency and a photolytic sensitivity that would not suit them for future practical applications. It is to be noted, however, that the more difficultly synthesizable analogues, having donor and acceptor groups separated by the ruthenium atom, have not been attained. It will be these types that test the expectations of the original proposal.

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A most satisfactory beginning has been made in this field here in our laboratory. Since we started, several other distinguished groups have begun working in the area, however, these groups are predominately staffed by physicists rather than chemists. We believe that our approaches as chemists compliment those of the other groups and we hope to continue work on the several important areas developed in this study.

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(16) The quantity minimized in refinement was:

$$\sum w(|F_o|-|F_c|)^2 \text{ , with } w = \frac{4F_o^2}{\sigma^2}.$$

The residuals are $R = \dfrac{\sum |F_o|-|F_c|}{\sum |Fo|}$, $wR = \dfrac{\sum w(|F_o|-|F_c|)^2}{\sum w|F_o|^2}$

goodness of fit $= \left[\dfrac{\sum w(|F_o|-|F_c|)^2}{(NO-NV)}\right]^{1/2}$.

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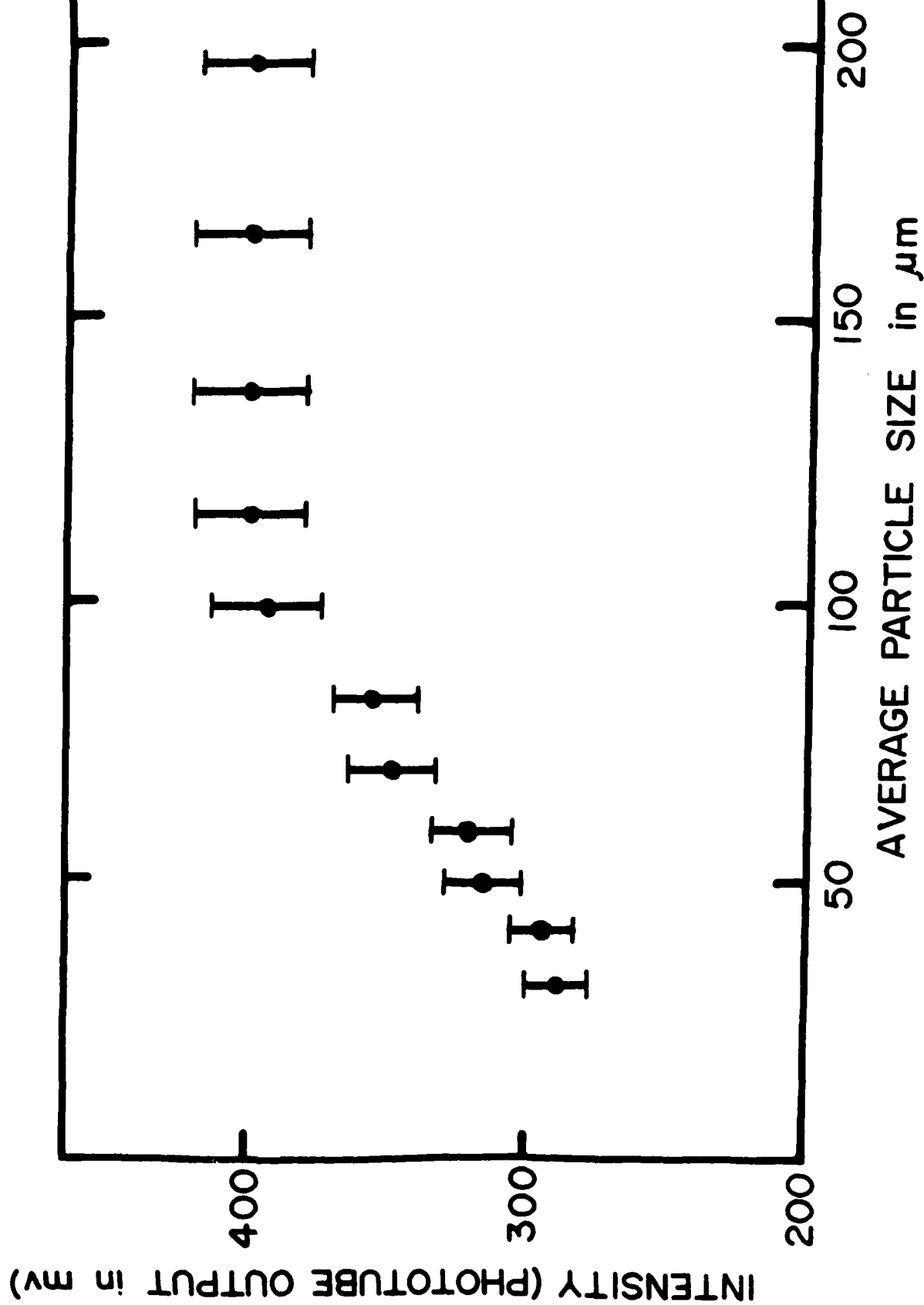(43)   See reference 35a, Vol. 2, Appendix II.

Figure Captions

Figure 1.   "Dependence of SHG Efficiency on Crystallite Size"

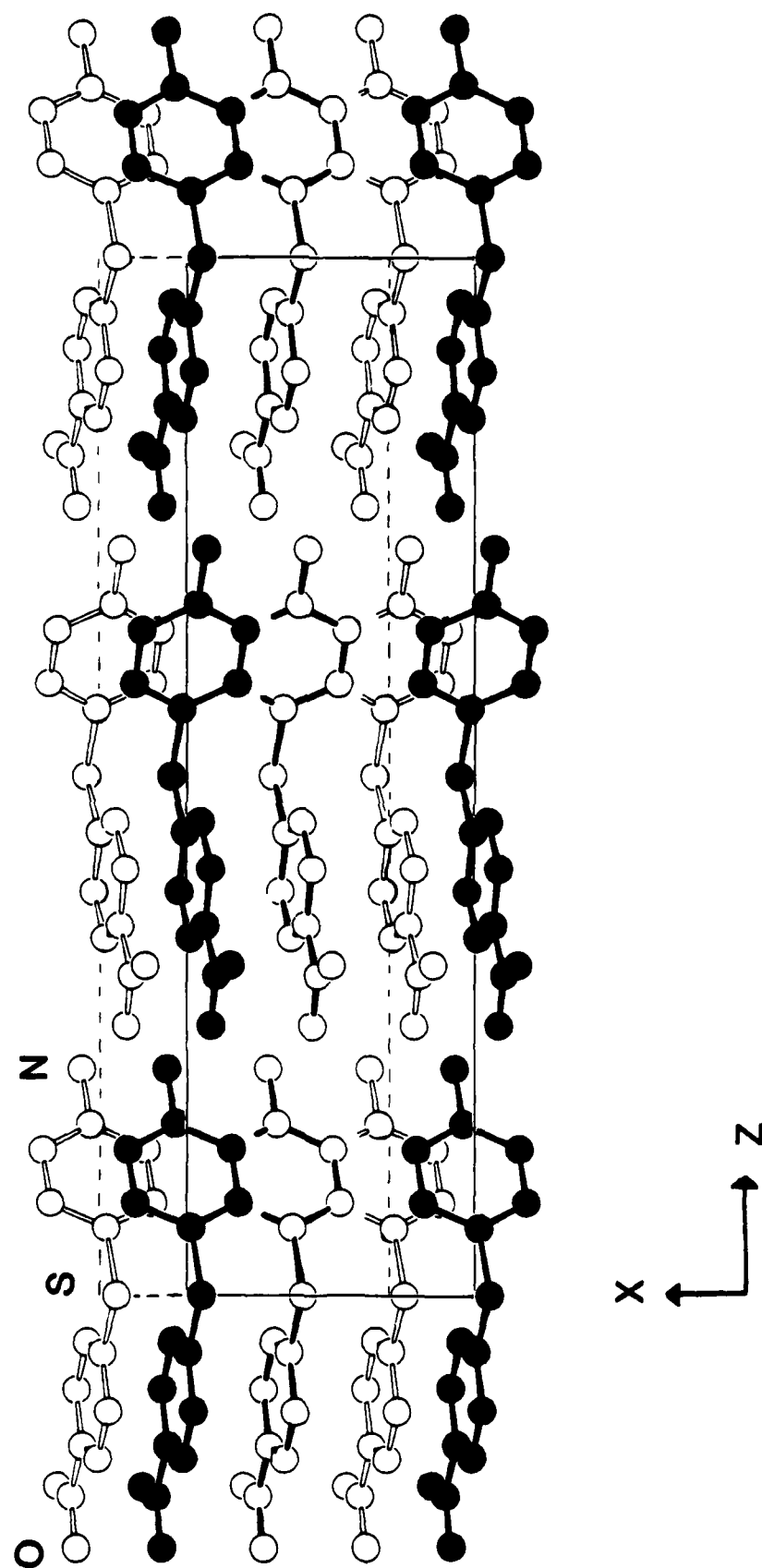Figure 2.   "Electronic Absorption Spectrum of ANDS in 1.0×10^4M Methanol Solution"

Figure 3.   "(010) Projection of the Unit Cell Contents of ANDS"

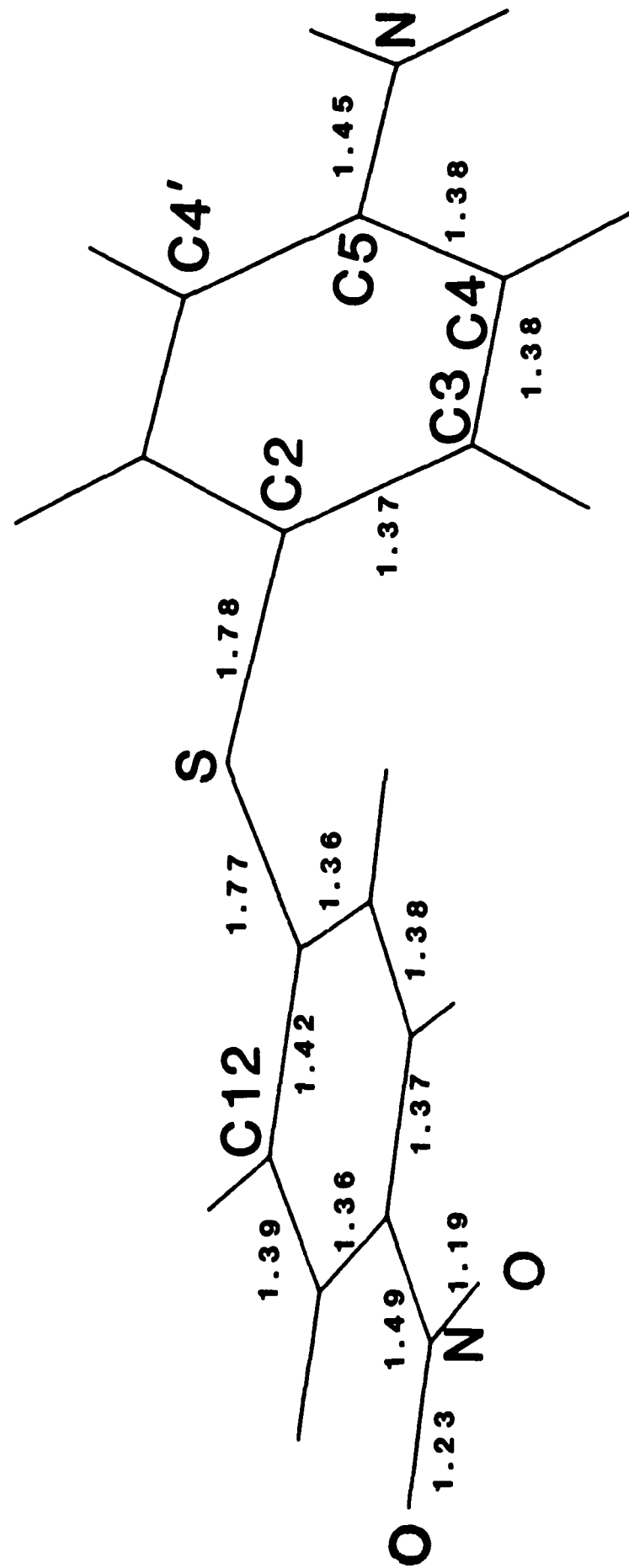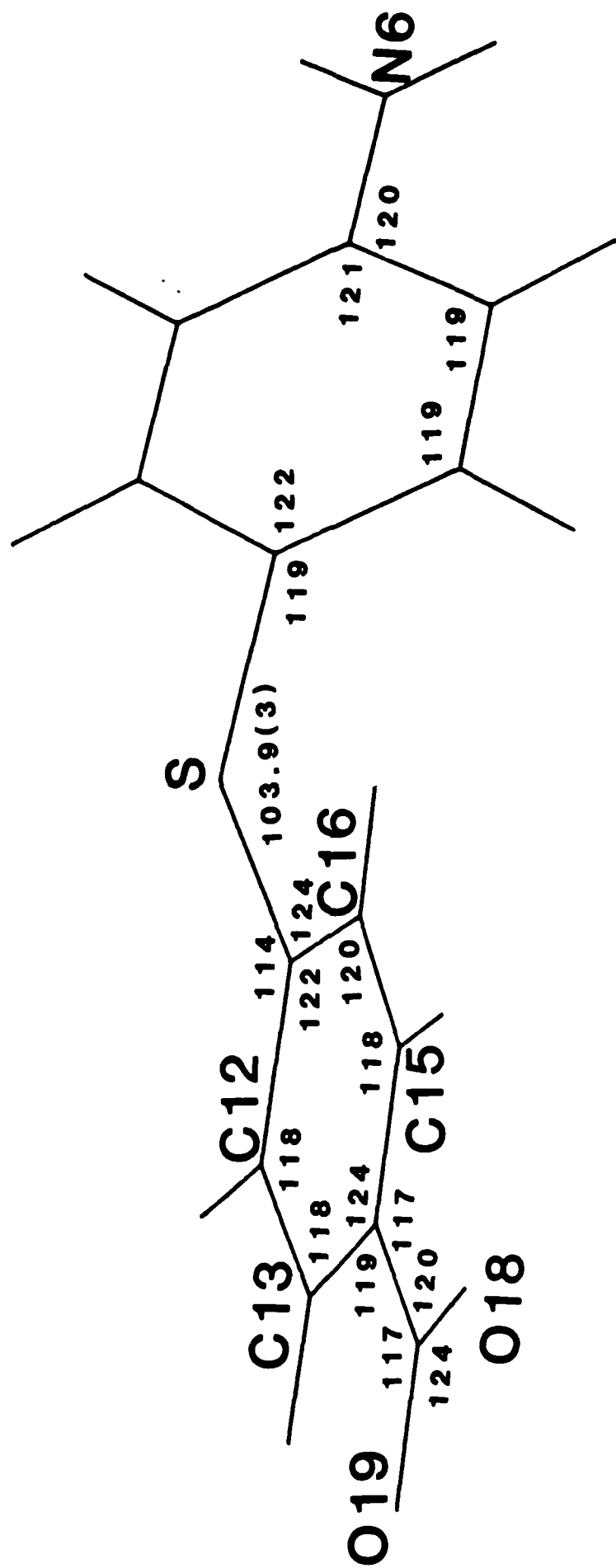Figure 4.   "(a) Bond Lengths and (b) Bond Angles"

Figure 5.   "Representation of the p_π Atomic Orbital Coefficients from the CNDO Calculation on the (a) HOMO and (b) LUMO. Diameters of Circles are Proportional to Orbital Coefficients."

Figure 6.   "(100) Projection with Some Molecules Removed for Clarity"

Figure 7.   "Electronic Absorption Spectra of NPP($-\cdot-$) and 6 ($-$) in Absolute Methanol at 25° C."

Figure 8.   "Absorption Cutoffs of 10^{-2} M Solutions in Absolute Methanol of NPP ($-\cdot-$) and 6 ($-$). ."

FIGURE 1. "DEPENDENCE OF SHG EFFICIENCY ON CRYSTALLITE SIZE"

FIGURE 2. "ELECTRONIC ABSORPTION SPECTRUM OF ANDS IN $1.0 \times 10^4 M$ METHANOL SOLUTION"

40

FIGURE 3. "(0,1,0) PROJECTION OF THE UNIT CELL CONTENTS OF ANDS"
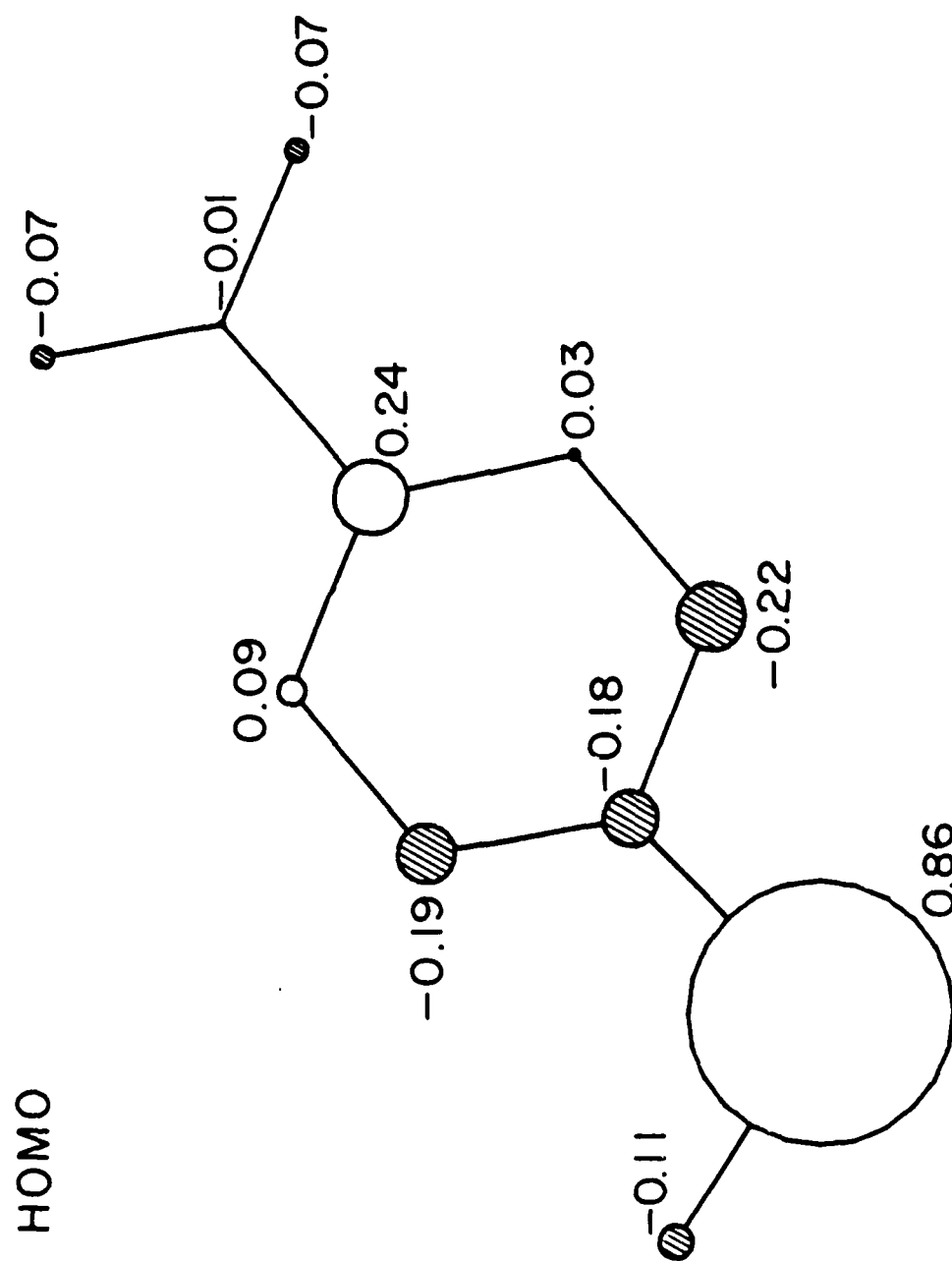
FIGURE 4A. "BOND LENGTHS"

FIGURE 4B. "BOND ANGLES"

HOMO

−0.07

−0.07

−0.01

0.24

0.03

0.09

−0.18

−0.22

−0.19

0.86

−0.11

FIGURE 5A. "REPRESENTATION OF THE P_π ATOMIC ORBITAL COEFFICIENTS FROM THE CNDO CALCULATION ON THE HOMO. DIAMETERS OF CIRCLES ARE PROPORTIONAL TO ORBITAL COEFFICIENTS."
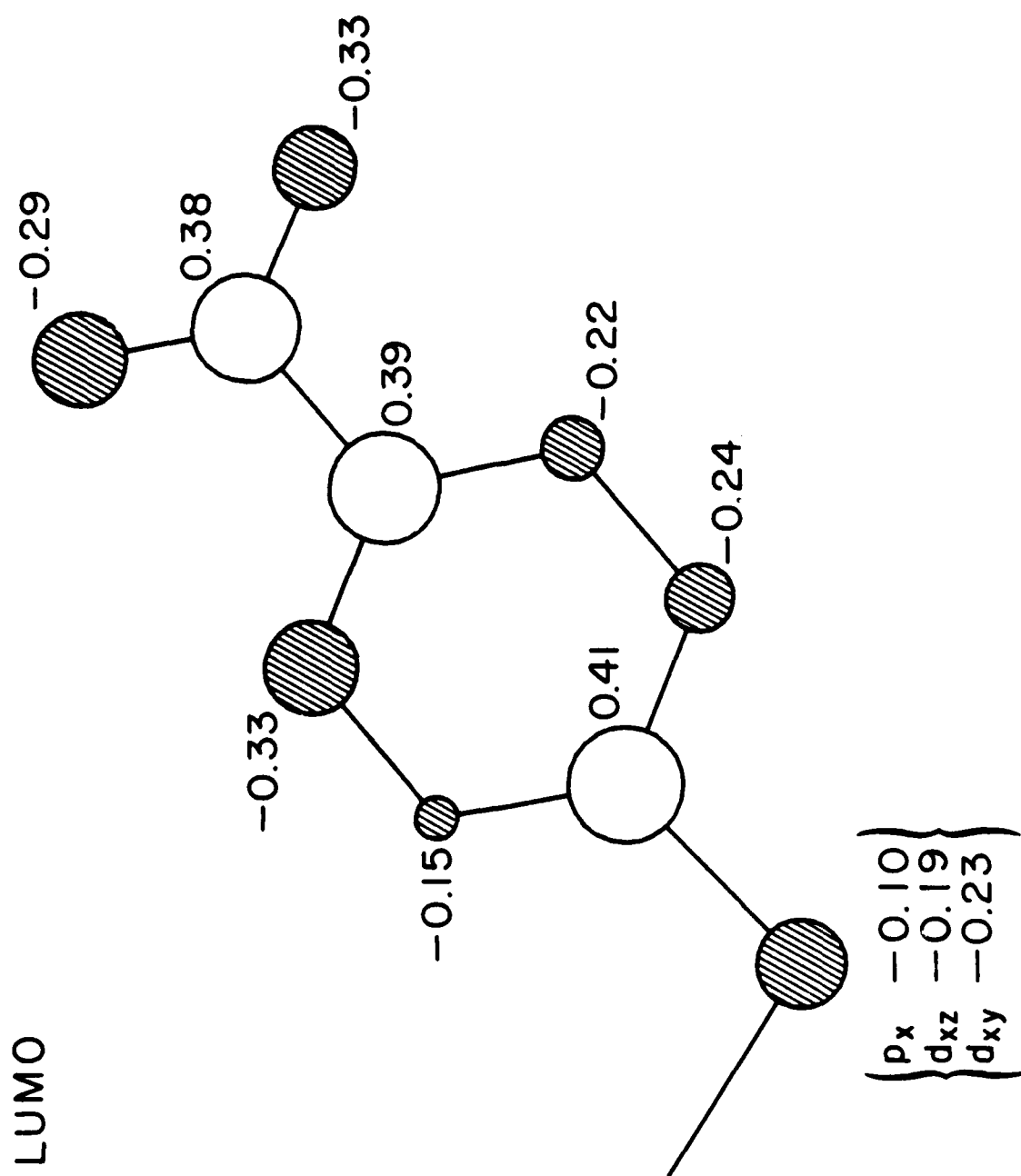
LUMO

$$\left\{\begin{array}{l} p_x \quad -0.10 \\ d_{xz} \quad -0.19 \\ d_{xy} \quad -0.23 \end{array}\right.$$

FIGURE 5B.   "REPRESENTATION OF THE P_π ATOMIC ORBITAL COEFFICIENTS FROM THE CNDO CALCULATION ON THE LUMO.   DIAMETERS OF CIRCLES ARE PROPORTIONAL TO ORBITAL COEFFICIENTS."
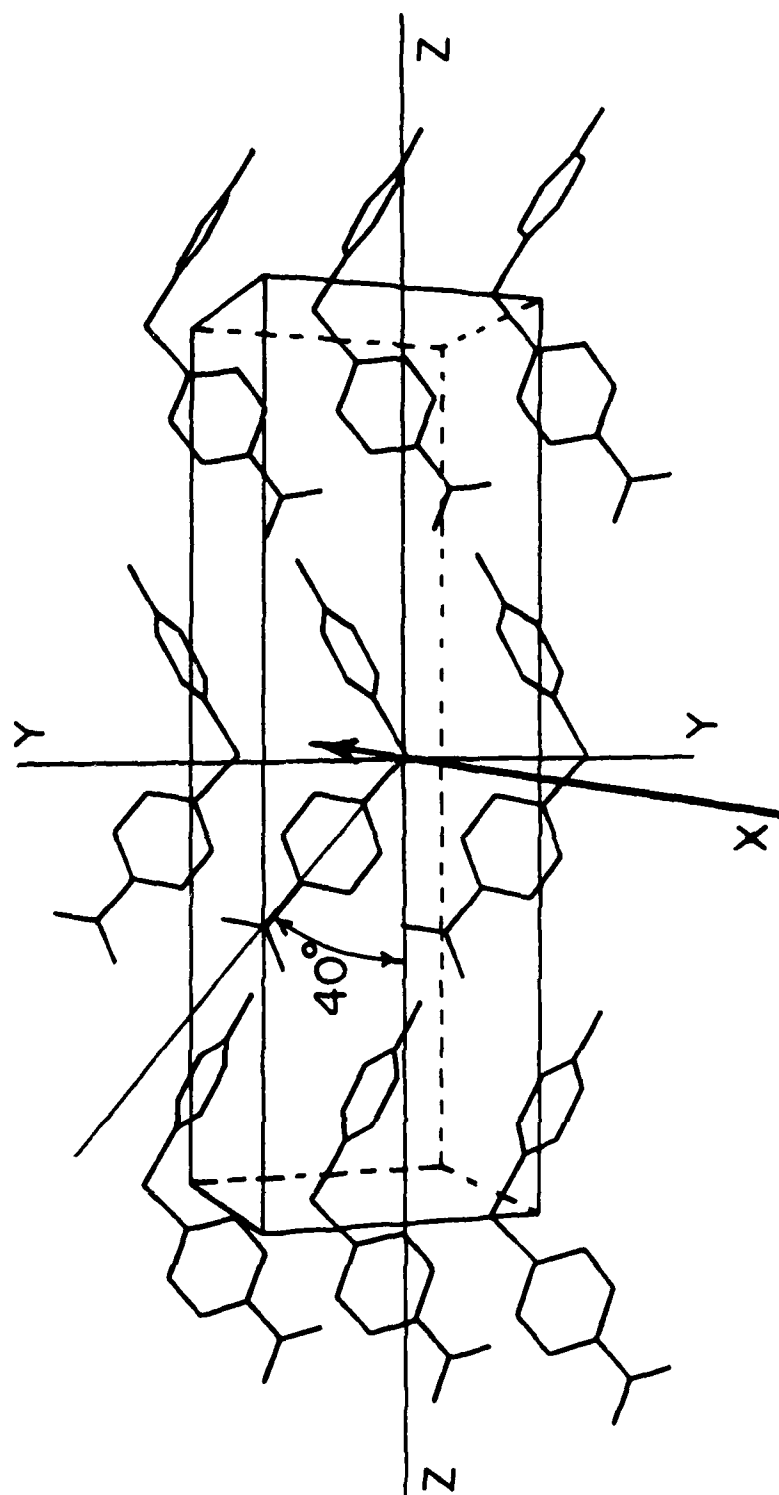
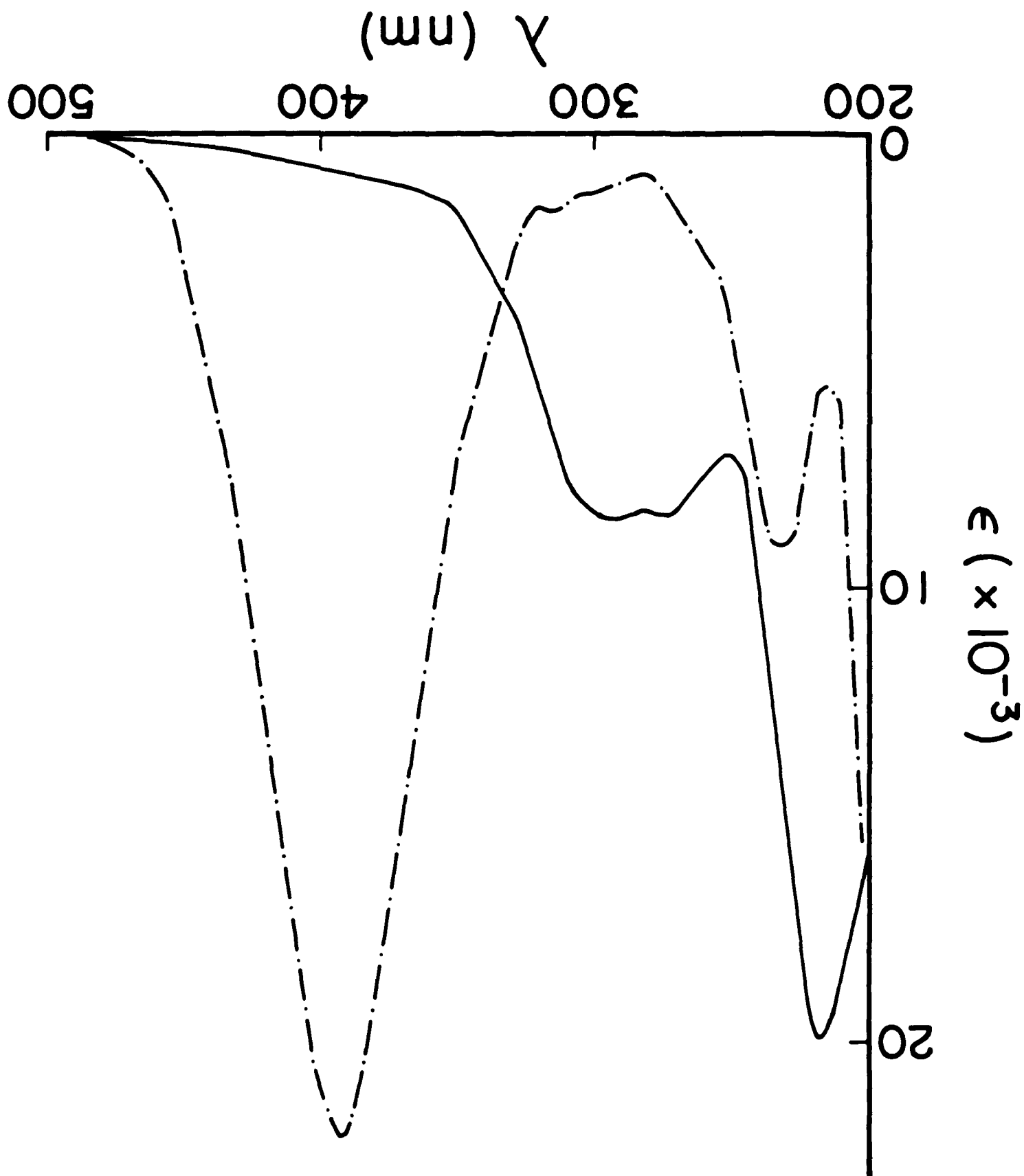FIGURE 6. "(100) PROJECTION WITH SOME MOLECULES REMOVED FOR CLARITY."

FIGURE 7. "ELECTRONIC ABSORPTION SPECTRA OF NPP (—·—)
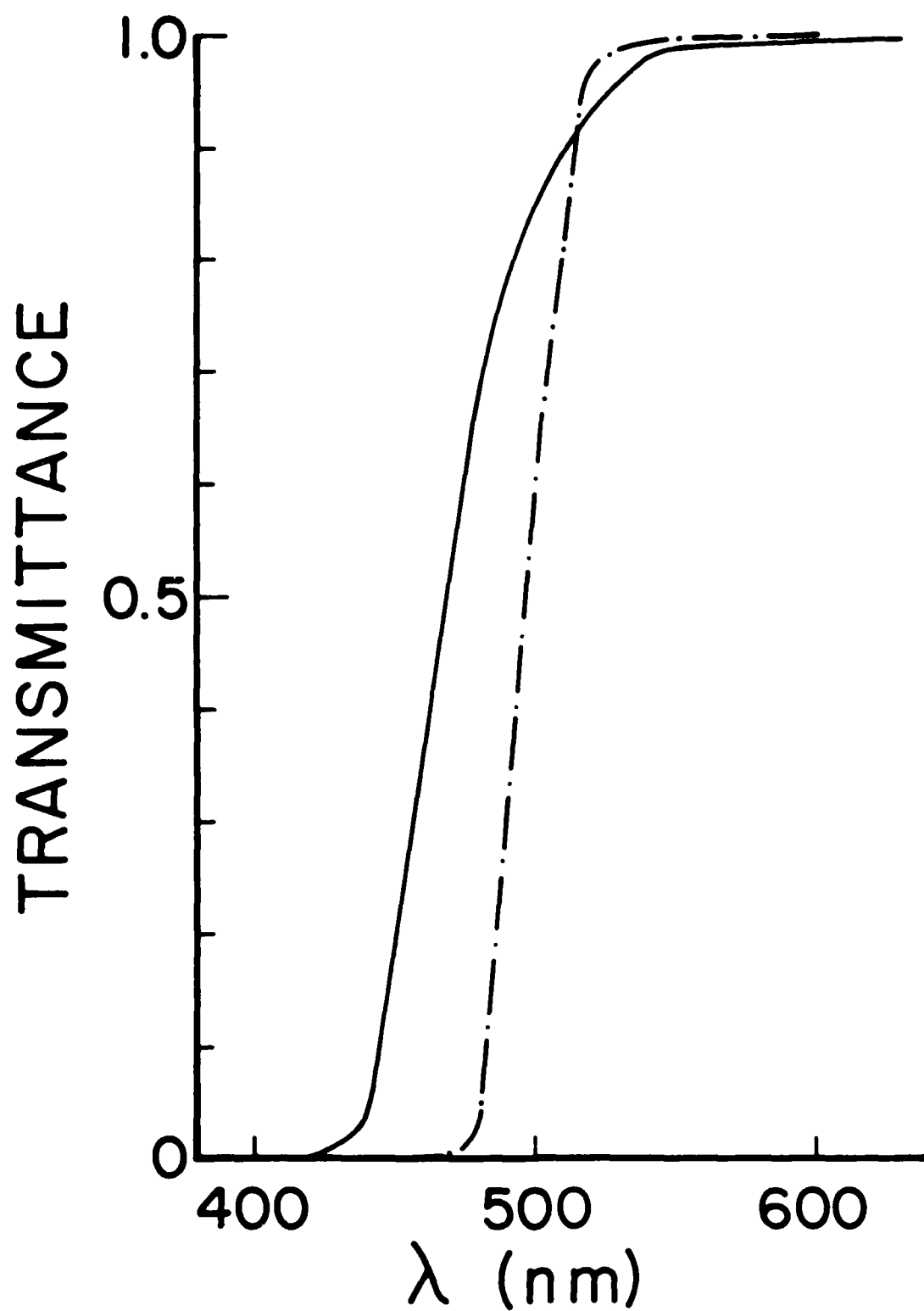AND 6 (——) IN ABSOLUTE METHANOL AT 25° C."

FIGURE 8. "ABSOPPTION CUTOFFS OF 10^{-2} M SOLUTIONS IN ABSOLUTE METHANOL OF NPP (−·−) AND 6 (——)."

Personnel and Publications

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PUBLICATIONS TO DATE:

"Preliminary Study of the Nonlinear Optical Properties of 4-Amino-4'-nitrophenyl Sulfide", H. Abdel-Halim, D.O. Cowan, D.W. Robinson, F.M. Wiygul, and M. Kimura, J. Phys. Chem. **90**, 5654 (1986).

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